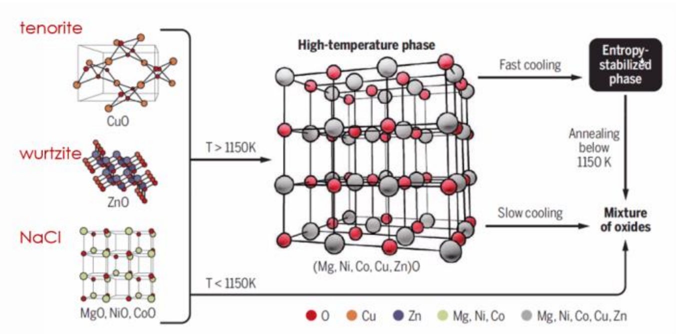
NÉEL INSTITUTE Grenoble

Topic for Master (M1 or M2) internship – Academic year 2023-2024

Exploring entropy-driven strategies to produce host matrices for Rare-Earth emitters

General Scope: High-Entropy Oxides (HEOs) represent a new paradigm in materials design with a large variety of compositions and crystal structures, and opportunities to achieve unique properties driven by synergistic effects between the combined elements. Until now, only scarce studies have addressed their interest for advanced optical ceramics. This project aims to fill this gap and explore entropy driven strategies for YAG ($Y_3Al_5O_{12}$), a rare earth host matrix used in lighting applications coupled with LED devices, or envisioned for biomedical imaging probes at the nanoscale. To this end, this internship will combine (1) solid-state syntheses to establish temperature-composition phase diagrams and understand the role of the mixing entropy on the reaction pathway, and (2) detailed structural characterizations and photoluminescence (PL) studies to quantify the influence of compositional and structural disorder on PL properties.

Research topic and facilities available: Since their discovery (Rost *et al.*, Nature 2015, figure below), entropy-stabilized oxides have become a promising playground to develop new functional materials, or address fundamental questions such as the role of chemical disorder on electronic, ionic or heat conduction. HEOs are generally produced by mixing several binary oxides, five or more, in near equimolar amounts. When heated at a temperature above which the configurational entropy dominates the Gibbs free energy term, a solid solution can be formed even from immiscible oxides, with the metal cations randomly distributed on the cationic sublattice of the structure.



Here, this concept will be adapted to form multielement oxides derived from YAG, whose crystallization temperature is about 850°C at ambient pressure. During this project, we will only consider substitutions in the A site of the $A_3B_2B'_3O_{12}$ structure. The impact of entropy will be addressed by measuring the onset temperature for the formation of a single garnet phase on heating and its dependency as a function of the total number of mixed components. For that, the usual method is to establish temperature-composition phase diagrams from reactions performed at the solid state using binary oxides as starting materials. Homogeneous mixtures of reactants (through planetary ball milling) will be treated by standard heat-dwell-quench sequences at increasing temperatures for a same dwell time and the single-phase character of the fired product will be controlled by *ex situ* powder x-ray diffraction (PXRD).

The influence of compositional and structural disorder on photoluminescence properties will be addressed by comparing well-crystallized samples synthesized at high temperature incorporating either 1, 2, 3, 4 or 5-cations on the A site doped with 1% Eu^{3+}. This disorder will be characterized using a wide range of techniques, from EDS coupled to SEM imaging for chemical mapping, PXRD or Raman spectroscopy, in addition to the PL studies. The intern will be trained to carry out all these measurements and to interpret the data obtained with the help of experts.

Possible collaboration/networking: D. Testemale (MRS research team, NEEL), A. Ibanez (OPTIMA, NEEL), C. Felix (POM, NEEL)

Possible extension as a PhD: not granted in advance, but we are open to support applications

Required skills: strong motivation for experiments and to broaden his/her scientific knowledge in material science and advanced spectroscopy techniques

Starting date: March 2024 or later (flexible).

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